



## **WATER RESOURCES RESEARCH GRANT PROPOSAL**

**Title:** Photocatalytic/Adsolubilization Semiconducting Monolith Reactor for the Treatment of Dilute Wastewater

**Focus Categories:** GW, TRT, WW

**Key Words:** Groundwater Quality, Hazardous Waste, Adsorption and Exchange, Industrial Wastewater, Wastewater Treatment, Organic Compounds

**Duration:** 3/1/99 to 2/28/00

**FY 1999 Federal Funds:** \$ 12,500

**FY 1999 Non-Federal Funds:** \$ 27,786

**Principal Investigators:** K.T. Valsaraj, Assoc. Professor, Dept. of Chemical Eng. W.D. Constant, Professor, Dept. of Civil & Environmental Eng. Louisiana State University, Baton Rouge, LA 70803

**Congressional District:** 6th

### **Statement of Problem**

A large fraction of the waste in the environment is in the form of highly dilute ground water and surface water. Despite gains made in pollution prevention, avoidance, and even awareness, contamination from non-point sources continues to be a problem. Agricultural runoff, aerosols, automobiles (combustion), house hold cleansers are some examples just to name a few. In many instances, the contaminants are organic, hydrophobic, and moderately nonvolatile in nature. Some examples include: polycyclic aromatic hydrocarbons (PAHs) emitted by coal gasification, petrochemical-related processes, and combustion processes; chlorinated aromatic hydrocarbons produced as insecticides or pesticides; and chlorinated phenols produced as fungicides and wood preservatives. Separating, recovering, or even destroying such compounds cheaply is a challenging problem.

In recent years, a large number of sites (Superfund sites) have suffered gross contamination by the release of anthropogenic substances into the natural environment. Although much of the contamination undoubtedly resulted from neglect, it is certainly reasonable to expect that non-point sources contributed to the problem. One of the largest Superfund sites (Petro Processors Inc. (PPI)), is located in Baton Rouge, Louisiana. Pump and Treat technology is the current method for treating the contaminated ground water at the site. Of the many unit operations used at the site, activated carbon adsorption is the preferred option for the treatment of dilute aqueous waste. This process suffers, however, in that it is nonselective and costly to regenerate the spent carbon. Additionally, activated

carbon is not necessarily as robust as one might think. Recently, in fact, PPI has suffered problems with their existing adsorption operation. It has been suggested that the carbon behaves catalytically to produce chlorinated VOCs by decomposition of higher molecular weight species. Therefore, developing a low-cost, reusable adsorbent process that is selective to simultaneous capture and destruction of hydrophobic organic compounds (HOCs) may overcome the disadvantages associated with activated carbon. Such a technology could save billions of Louisiana, tax payer dollars. Additionally, such a technique could be used in the local Chemical Process Industry (CPI) as a new means of pollution prevention.

### **Statement of Results, Benefits, and/or Information**

We foresee a treatment alternative that employs a natural or commercial surfactant supported on semi-conducting monolithic reactors made of titania. The role of the surfactant is to selectively scavenge HOCs from dilute aqueous streams and concentrate them at the titania surface. Fiber optic cables, transmitting ultraviolet radiation, are used to promote the simultaneous photocatalytic destruction of the adsorbed HOCs. Our previous adsolubilization work (Valsaraj, et. al., 1998) has shown that sodium dodecyl-sulfate-modified alumina not only has a large sorptive capacity for PAHs, but it is also easily regenerable by moderate changes in pH. This was the object of the past research from our group which was also funded by LWRRI. It is reasonable to expect that titania, a similar mineral oxide, will show equivalent sorptive equilibria. Since it has been shown that surfactants serve as hydrogen donors in homogeneous photolysis and improve quantum yields (Shi et. al., 1997), it is reasonable to assume that the same phenomenon may occur in a heterogeneous system. In effect, we expect that the combination of adsolubilization with ultraviolet photocatalysis results in the simultaneous separation and decomposition of the HOCs. This will benefit the PPI superfund site as well as others because the new treatment scheme will be compound selective, easier to regenerate, and more efficient in the removal and destruction of organic compounds.

### **Nature, Scope, and Objectives of the Research**

The treatment of dilute aqueous streams continues to be at the forefront of environmental and chemical process R&D efforts (NRC, 1988). This is mainly due to two reasons: (1) the relative abundance of the streams; they are found literally everywhere in the CPI, municipal treatment facilities, natural environment, etc. and (2) the exponentially growing number of environmental laws regulating pollution emission. The costs to treat the streams have followed an exponential growth as well. Moreover, in many cases, the type of treatment utilized (air stripping or activated carbon etc.) only changes the nature of the problem rather than solving it. Since we cannot affect the relative abundance of the streams without sacrificing the quality of life we have all been accustomed to, we must focus on reducing the costs of treatment. One way in which this can be done is to explore new ways in which developing technologies can be combined to overcome current limitations. In this proposal, it is suggested that a combination of photocatalysis and adsolubilization in a novel monolithic reactor design can overcome the problem of low conversions observed in conventional photocatalytic reactors and the problem of short breakthrough

times in adsolubilization. This proposal draws upon areas in photolytic physics, chemistry, hydrodynamics, and chemical engineering. The main goal of this research is to develop a comprehensive treatment technology for groundwater aquifers using surfactant solutions.

### Adsolubilization

Adsolubilization (Fitzgerald et. al., 1986) is a low energy separation process which uses surfactant-modified mineral oxide particles (e.g.  $\gamma$ -alumina) to selectively remove HOCs. Surfactant is brought into contact with the alumina by flowing a dilute aqueous solution through a packed bed. The amount of surfactant adsorbed is dependent upon the pH. For anionic surfactants such as, sodium dodecyl sulfate (SDS), loading increases with decreasing pH and, in general, is nonlinearly related to the bulk concentration (Valsaraj et. al., 1998a). However, for dilute solutions at constant pH, the equilibrium relationship governing the distribution of surfactant is linear,

The tails of the bound surfactant molecules aggregate into "hemimicelles" and provide nonpolar sites into which the HOC may "adsolubilize". The amount of HOC adsolubilized is dependent upon the type of HOC, the amount of surfactant bound, and the bulk phase HOC concentration,

Here,  $K_h$  is the surfactant normalized sorption constant. We have shown in our laboratory that for SDS,  $K_h$  is related to the octanol-water partition coefficient by the expression, (Valsaraj et. al., 1998a). Because of the strong dependence of  $K_h$  on  $K_{ow}$ , adsolubilization is particularly useful for separating hydrophobic organic molecules, such as polynuclear aromatic hydrocarbons, chlorinated aromatic hydrocarbons, and other related compounds. Model predictions and laboratory experiments (Smith and Valsaraj, 1998; Valsaraj et. al., 1998b) conducted with packed beds containing alumina particles have illustrated this phenomenon

### Photocatalytic Degradation of Aqueous Borne Organics

Photocatalytic degradation of aqueous borne pollutants is a technique in which UV/Vis (300-500 nm) radiation delocalizes a valent electron to the conduction band of semiconductors e.g.  $\text{TiO}_2$ , CdS, ZnO, SiC, etc. (Hoffman et. al., 1995). The photoexcited electron-hole pair then initiates the decomposition of adsorbed species by one or more forms of electron transfer (Linsebigler et. al., 1995; Bard, 1980). Figure 1 illustrates the well accepted mechanism for  $\text{TiO}_2$ . The two opposing steps are recombination and electron transfer. Recombination of the photoelectron-hole pair is undesirable and can occur either in the bulk or on the surface of the semiconductor. Electron transfer requires an electron acceptor ( $\text{O}_2$ ) for the photoelectron and an electron donor (or hydrogen source) for the (+)hole. In Figure 1, the (+)hole is assumed to be trapped within defects upon the  $\text{TiO}_2$  surface (interfacial charge transfer) such as,

Such a low value explains why much of the effort in this field is focused on ways of improving the quantum yield. Variables which have been investigated include: the type

of the mineral oxide, metal doping of the mineral oxide (Pt, Fe(III), Cr(III), or Ag) to assist in e<sup>-</sup> trapping, incident light intensity, porosity of aggregates, donor species concentration, competitive sorbates, pH, and temperature (Hoffman et. al., 1995; Linsebigler et. al. 1995).

One interesting means of improving the quantum yield is by the addition of a surfactant. Chu and Jafvert (1994) have reported an order of magnitude increase in quantum yield with the addition of a nonionic surfactant to dissolved hexachlorobenzene. Additionally, Shi et. al. (1997) have reported on the homogeneous photochemical degradation of 2-chlorophenol in dissolved surfactant solutions. For surfactant (sodium dodecyl sulfate, SDS) concentrations below the CMC, they observed 10-50% increases in quantum yield over surfactant-free solutions. Since the reaction did not involve a mineral oxide, they attributed the enhancement to the additional hydrogen source (donor).

As the mechanism of photochemistry appears to be well understood, perhaps the most important area of research is the design of the photoreactor itself. For any practical application, a cheap and efficient means of irradiating the mineral oxide is required. Slurry, fluidized-bed, and other batch reactors are avoided as they increase the cost due to post liquid-solid separation steps. Reactors involving immobilized catalyst appear to be the current direction of research (Hoffman et. al., 1995). For instance, Serrano and de Lasa (1997) have introduced the Photo-Chemical Reactor Engineering Centre reactor, abbreviated as Photo-CREC. Recognizing the need to properly illuminate immobilized catalyst, the authors constructed a 16 staged concentric reactor with a 2.8 liter holdup. TiO<sub>2</sub> was impregnated on a glass mesh which surrounded a 15-W monochromatic lamp ( $\lambda=365$  nm). With methylene blue as their target compound, they determined the quantum efficiency to be 6.3% of the ideal Photochemical Thermodynamic Efficiency Factor (PTEF). The ideal PTEF is defined as

where  $\phi = 94$  KJ/mol. The PTEF is based on the mechanism of hydroxyl radical formation from either a photoelectron or hole trapped in a surface defect. Equation (4) represents the upper limit; thus, factors such as fluid dynamics, mass transfer, and light absorption or scattering reduce the value. Serrano and de Lasa (1997) provide an additional quantum yield factor to account for such factors. However, effects of catalyst can offset these somewhat. For instance, using the quantum yield estimated by Equation (3), one can calculate the quantum efficiency for the heterogeneous TiO<sub>2</sub> system to be 16.6% of the ideal PTEF. It appears then that the PTEF is an appropriate measure of reactor performance. It should be noted however that the quantum yield may also be calculated by (Chu and Jafvert, 1994)

where  $k_{app}$  is the apparent first order rate constant,  $I_0$  is the luminous intensity,  $\epsilon$  is the molar absorptivity, and  $l$  is the cell path length. Because an apparent first order rate constant is used Equation (5), the quantum yield reflects all possible mechanisms of decomposition, not just that by OH<sup>•</sup> attack, as assumed in Equation (4). Thus, predictions from Equation (5) may be greater than those by Equation (4).